Radiocarbon dating of Methane

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Torben Gentz, Malte Hoehn, Hendrik Grotheer, Sabine Kasten and Gesine Mollenhauer
Contact: Torben.Gentz@awi.de/ Malte.Hoehn@awi.de

1 Introduction

Methane (CH_4) is the most abundant organic compound in the atmosphere and its impact on the global climate is subject of numerous scientific studies (e.g. Saunois et al, 2020). The origin of methane (biogenic or thermogenic) can be determined by $^{13}C/^{12}C$ ratio measurements (Whiticar, 1999). However, several important methane releasing processes resulting from anaerobic degradation of organic material in ocean sediments and permafrost soils are not yet fully understood (e.g. Knoblauch et. al, 2018). Radiocarbon dating has the potential to provide new insights on methane sources and pathways of its cycling, in particular in settings with high methane concentrations including sediments and permafrost.

Here we present our new developed method for ^{14}C analysis of natural high-concentration methane samples with the main requirements of efficient gas separation, long term sample storage and subsequent transfer to MICADAS excluding any contamination.

2 Method

Required sample	• Gas mix • High CH_4 concentration preferred • Target sample size 100µg C
PreCon (modified)	• Separation and storage of gas mix and CH_4 oxidization (fig. 2) • Loading of mobile zeolite traps (fig. 1) with sample CO_2 (Trap A) and oxidized CH_4 (Trap B)
GIS/MICADAS	• Coupling of sample loaded mobile trap to GIS (fig. 3) • Desorption of sample and measurement at MICADAS

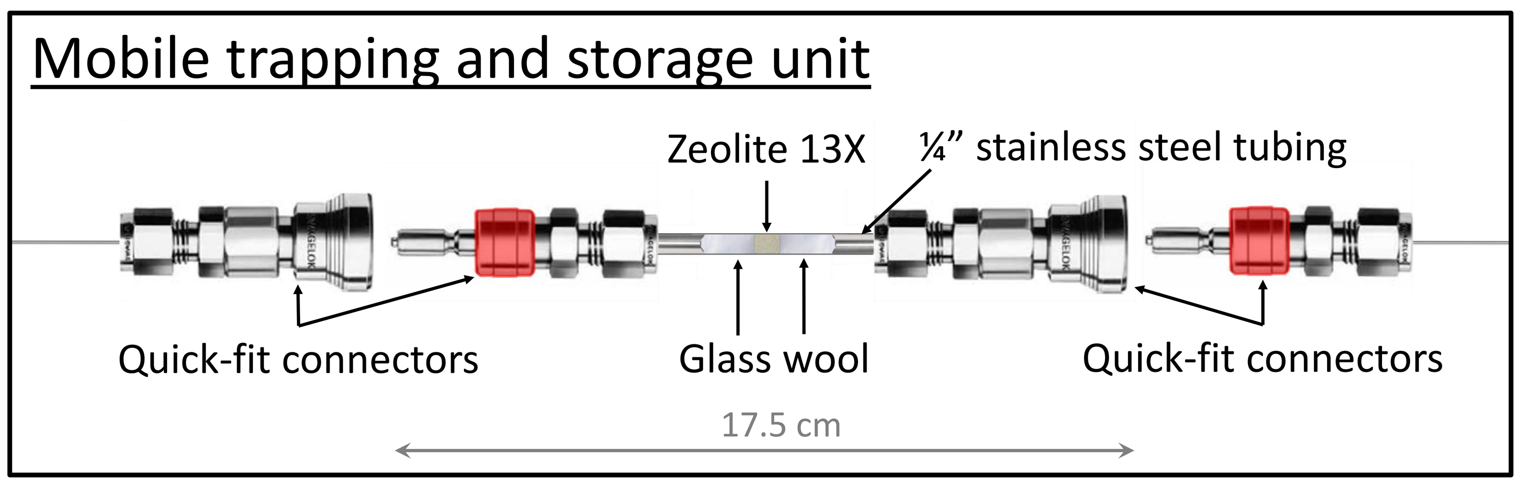

Fig. 1: Schematics of a self-made, mobile zeolite trap (Wotte, 2017); CO_2 is loaded on a trap in a stream of helium gas; quick-fit connectors allow easy coupling to various instruments.

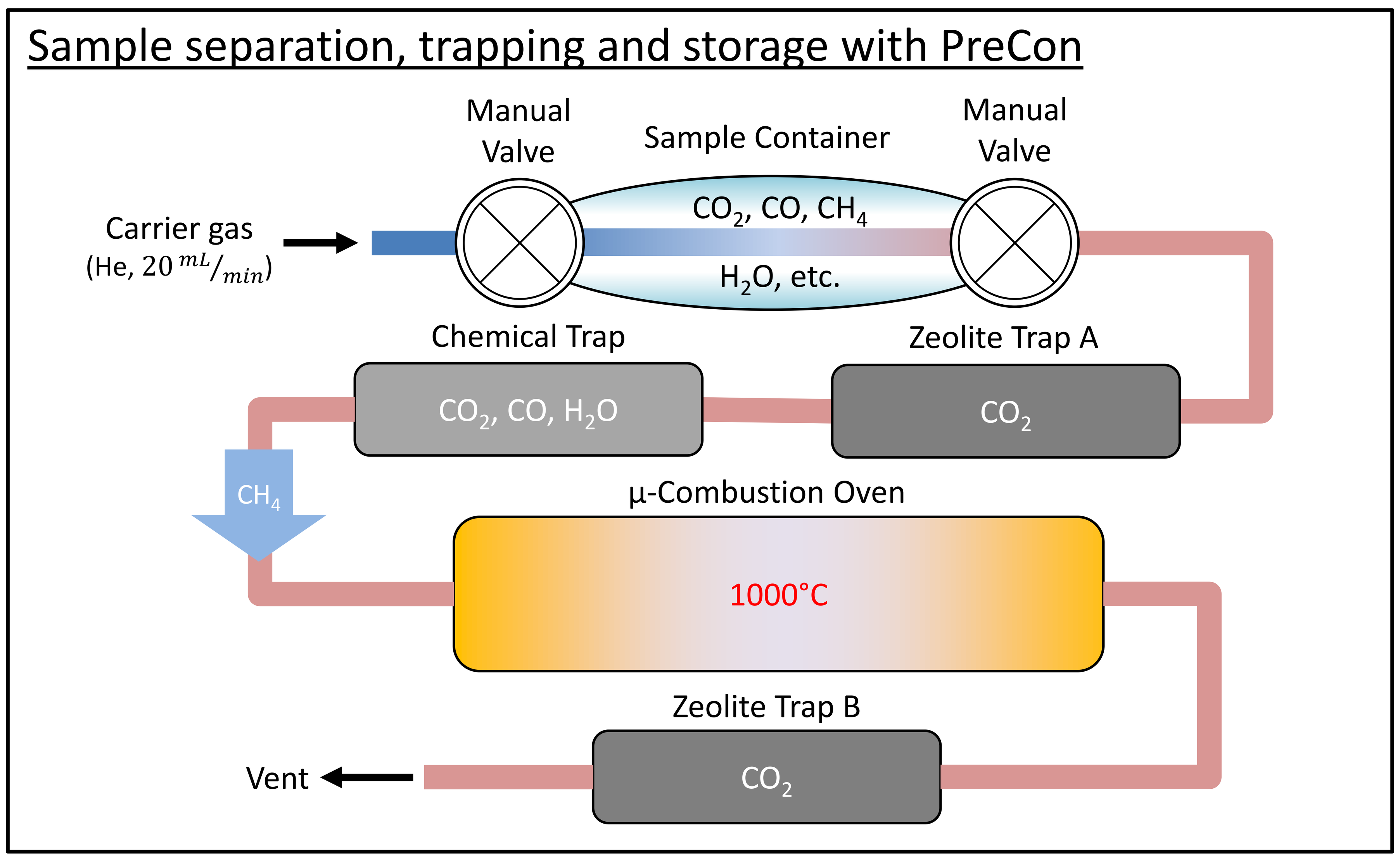

Fig. 2: Schematics of the preparation unit (modified PreCon, Thermo Fischer); a sample is injected into the sample container. CO_2 is collected on trap A, CH_4 is combusted in the modified PreCon combustion oven and collected on trap B. Both traps are subsequently disconnected and can be re-connected to the sample injection unit.

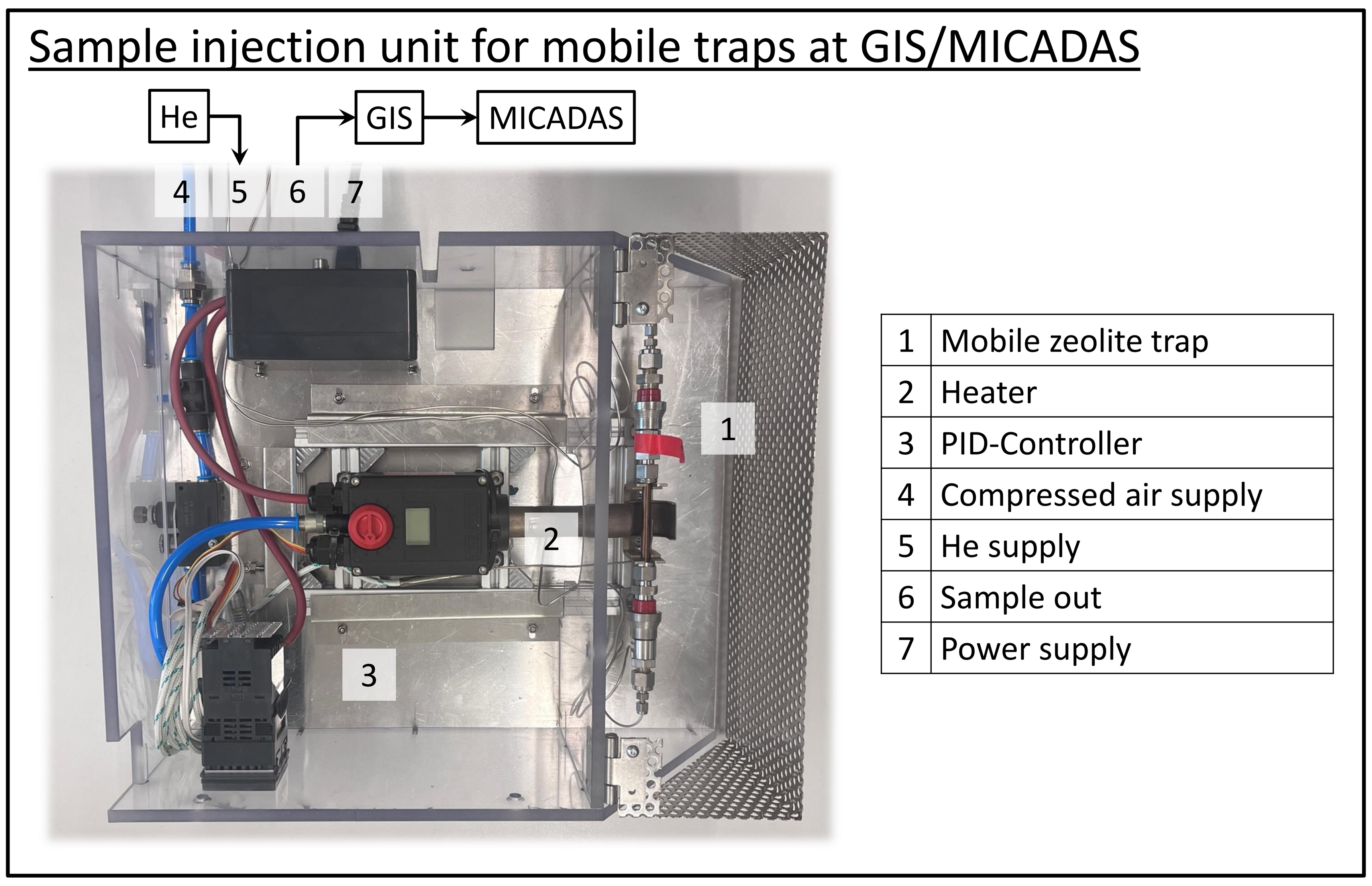

Fig. 3: Mobile trap assembly at GIS/MICADAS; CO_2 loaded traps can be attached using quick-fit connectors, CO_2 is thermally desorbed and transferred to the injection system of GIS.

3 Results

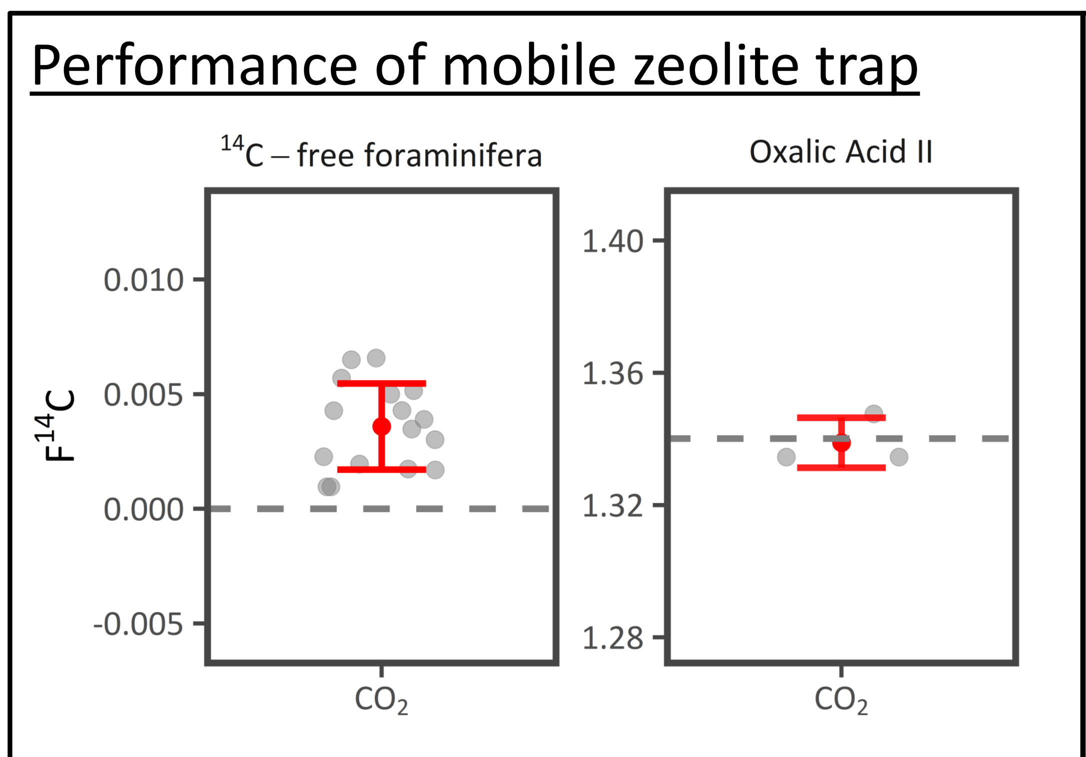

Fig. 4: Proof of replicability and potential contamination: Zeolite traps were loaded with CO_2 gas produced by acid hydrolysis of ^{14}C-free foraminifera with CHS-GIS/MICADAS (carbonate; $F^{14}C=0$) and from oxalic acid II ($F^{14}C=1.34$) standard.

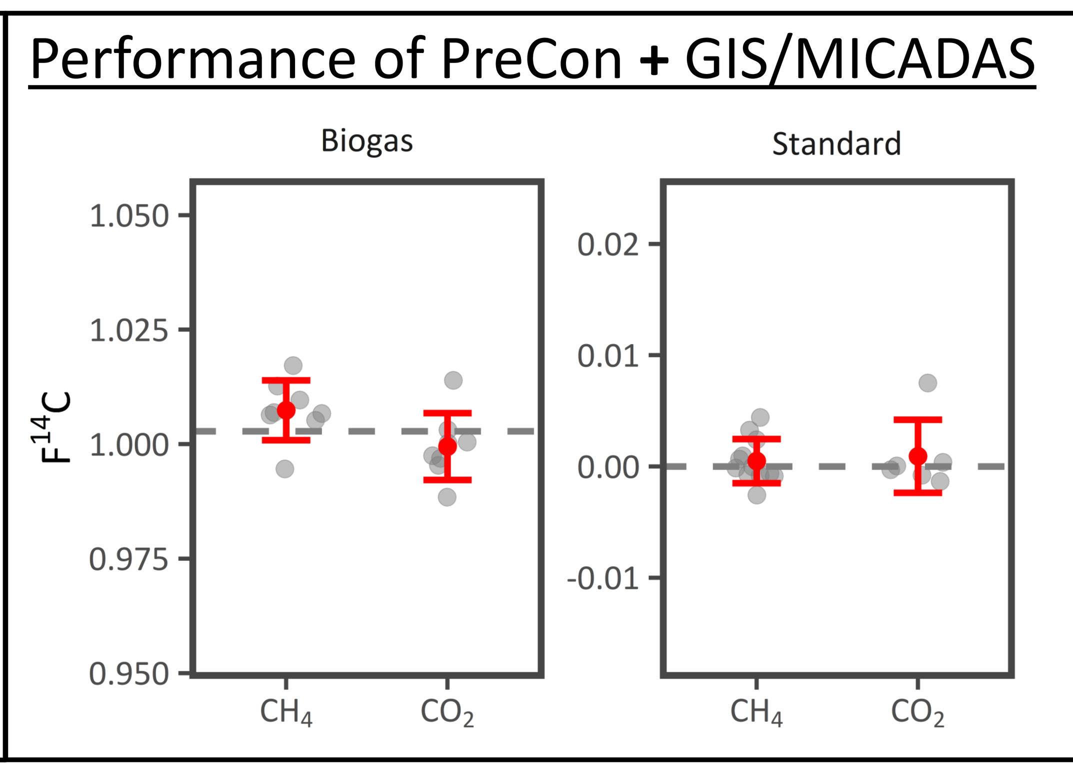

Fig. 5: Replicability of modern and ^{14}C-free CO_2 and CH_4 gases: Biogas containing CO_2 and CH_4 and was produced from organic matter with $F^{14}C=1.01$.

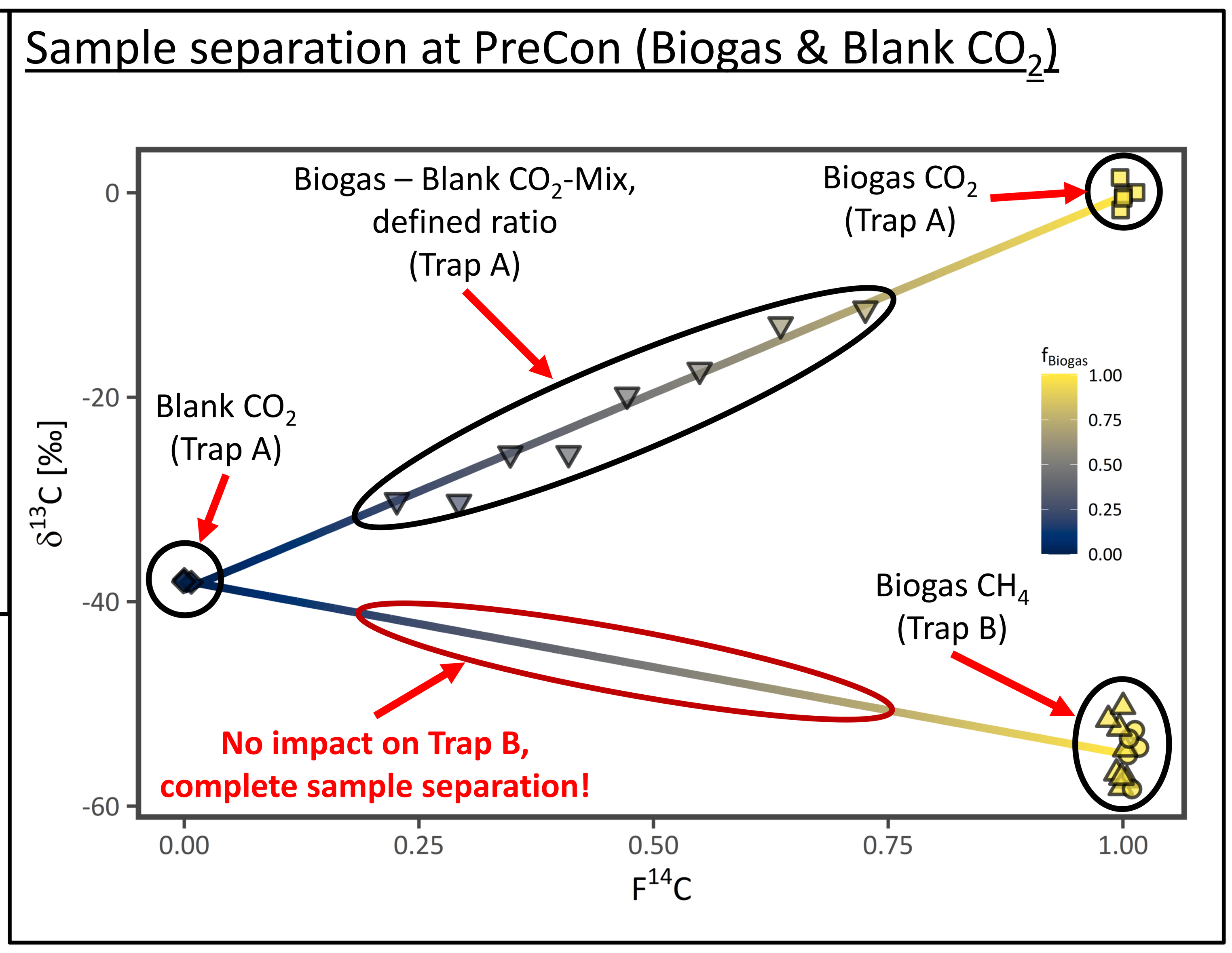

Fig. 6: Sample separation efficiency of the setup was tested by determining $F^{14}C$ and $d^{13}C$ in various mixed samples containing defined ratios of biogas ($F^{14}C$ = 1.01; 53% CH_4, 47% CO_2) and ^{14}C-free CO_2 ("blank CO_2"; 100% CO_2, $F^{14}C$ = 0).

4 Conclusion

- Mobile zeolite traps works comparable to GIS/AGE trapping system
- Low sample size requirement (down to 20µg)
- Complete gas separation (CO_2 and CH_4) by modified PreCon
- No contamination during sample transfer to GIS/MICADAS observed

References
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Wotte, A, et. al (2017) $^{14}CO_2$ processing using an improved and robust molecular sieve cartridge. Nuclear instruments and Methods in Physics, Research Section B: Beam Interactions with Materials and Atoms, 65-73, doi: 10.1016/j.nimb.2017.04.019

ALFRED-WEGENER-INSTITUT
HELMHOLTZ-ZENTRUM FÜR POLAR- UND MEERESFORSCHUNG
HELMHOLTZ GEMEINSCHAFT
BREMERHAVEN
Am Handelshafen 12
27570 Bremerhaven
Telefon 0471 4831-0
www.awi.de